

REMARKS

Reconsideration is respectfully requested in view of the above amendments and the following remarks.

35 USC 112, Second Paragraph

Claims 33, 39-43 stand rejected under 35 USC 112, second paragraph.

The Action states that there is insufficient antecedent basis for “the reaction mixture” in claim 33. Claim 33 has been amended to remove reference to the “reaction mixture.” Claim 33 is now rewritten in independent form.

Claim 36 is stated to be confusing. Applicants have amended the claim to recite that the 1,3-propanediol reactant consists essentially of the 1,3-propanediol and the 1,3-propanediol has a purity greater than 99%. Applicants submit that the amended claim is proper.

Claim 37 is stated to be incomplete. Applicants have amended claim 37 to state that the 1,3-propanediol reactant comprises the 1,3-propanediol and up to 10% of the low molecular weight oligomers or prepolymers. Applicants submit that the amended claim is proper.

Claim 39 is stated to improperly refer to a mixture as containing one element. Applicants have amended claim 39 to remove the reference to the mixture containing one element. Applicants submit that the revised claim is proper.

For the above reasons, withdrawal of the rejection under 35 USC 112, second paragraph, is respectfully requested.

35 USC 102(b)/35 USC 103(a) - US 3,326,985 Mason et al.

Claims 1-6, 9-14, 16, 20-22, 37 and 44 stand rejected under 35 USC 102(b) as anticipated by US 3,326,985 Mason et al (“Mason”). Claims 26-28 stand rejected under 35 USC 102(b) as anticipated by or, in the alternative, under 35 USC 103(a) as obvious over Mason.

The process claims are directed to carrying out a polycondensation reaction at less than one atmosphere, whereas D1 teaches carrying out a polycondensation reaction at stand pressure and then vacuum stripping. Here, it is noted that the invention includes the process of precondensing to form the oligomers or prepolymers of 1,3-propanediol having a degree of polymerization of 2-9 and then condensing the polymer.

Claim 1 is directed to a process for the manufacture of polytrimethylene ether glycol comprising the steps of:

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- a) providing (1) 1,3-propanediol reactant selected from the group consisting of 1,3-propanediol and/or oligomers or prepolymers of 1,3-propanediol having a degree of polymerization of 2-9 and mixtures thereof, (2) a polycondensation catalyst, and (3) 20 weight % or less of comonomer diol; and
- b) polycondensing the 1,3-propanediol reactant to form a polytrimethylene ether glycol at less than one atmosphere pressure.

Claim 39 is directed to a process for the manufacture of polytrimethylene ether glycol comprising the steps of:

- a) providing (1) 1,3-propanediol, (2) a polycondensation catalyst and (3) up to 20 weight % or less of comonomer diol;
- b) condensing 1,3-propanediol to form oligomer or prepolymer of 1,3-propanediol having a degree of polymerization of 2-9 or a mixture thereof; and
- c) polycondensing the oligomer or prepolymer of 1,3-propanediol having a degree of polymerization of 2-9 or a mixture thereof, to form a polytrimethylene ether glycol at less than one atmosphere pressure.

Mason is cited in the Office Action as teaching a process for producing polytrimethylene glycol (PO3G) comprising "precondensing it at the atmospheric pressure and then further condensing it at very low pressure (1 to 8 mm) at a temperature above 150 and below 250 C."

The process claims are **not** anticipated by D1 for two primary reasons.

- (1) The present invention is directed to polymerizing at low pressure, whereas D1 is directed to forming polymer at atmospheric pressure and then vacuum stripping.
- (2) The starting material of the invention is different than the starting material used in the vacuum stripping process of D1.

For expediency, Applicants will not go into the many other reasons the claims are not anticipated.

Mason is described in the subject application as follows:

"U.S. Patent No. 3,326,985 discloses a process for forming a polytrimethylene glycol having an average molecular weight of 1,200-1,400. First, polytrimethylene glycol which has an average molecular weight of about 900 is formed using hydriodic acid. This is followed by an after treatment which comprises vacuum stripping the

polyglycol at a temperature in the range of 220-240°C and at a pressure of 1-8 mm Hg in a current of nitrogen from 1-6 hours. The product is stated to be useful in preparing polyurethane elastomers. There is also presented a comparative example directed to producing polytrimethylene glycol with a molecular weight of 1,500.”

The process claims are directed to carrying out a polycondensation reaction at less than one atmosphere, whereas Mason teaches carrying out a polycondensation reaction at stand pressure and then vacuum stripping. That is, in the invention 1,3-propanediol and/or oligomers or prepolymers of 1,3-propanediol having a degree of polymerization (DP) of 2-9 is polymerized to form polytrimethylene ether glycol at less than one atmosphere pressure. This process provides a higher yield than the process described in Mason. Mason teaches a process comprising forming a polytrimethylene ether glycol having an average molecular weight of 900 and then vacuum stripping the polytrimethylene ether glycol. The vacuum stripping step of Mason is not a polycondensing reaction. Mason is teaching a process where low molecular weight species (e.g., unreacted 1,3-propanediol, dimers and trimers) are removed by vacuum stripping. Thus, Mason is simply removing lower molecular weight species to get a higher average molecular weight of the polyol. To support applicants position, the Examiner is directed to column 2, line 2, of Mason wherein the vacuum stripping procedure is described as an “after treatment.” Consequently, Mason does not teach or suggest the claimed process or resultant products.

Concerning distinction (2), 1,3-propanediol with a DP of 9 would have a MW of 540. ($DP = (58 \times \text{number of repeat units}) + 18$.) Thus, the claimed starting material has a lower molecular weight than the materials used in the vacuum stripping of Mason. Also, note that while the claims refer to DPs of 2-9, the general reaction preference is to start with either 1,3-propanediol, dimer and trimer (dimer and trimer would have $DP \leq 3$) as in claims 2-4.

Product claim 44 was amended to recite that the PO3G has a molecular weight greater than 1,500. This claim is patentable since highest MW shown in Mason is 1,400. Example 2 of Mason is referring to a molecular weight of 1,500, but that is a calculated value and the actual value is much lower.

For the above reasons, withdrawal of the rejections under 35 USC 102 and 103 is respectfully requested.

35 USC 103(a) - US 5,403,912 Gunatillake et al.

Claims 1-49 stand rejected under 35 USC 103(a) over US 5,403,912 Gunatillake et al. (“Gunatillake”). Gunatillake is cited as disclosing a process of manufacturing polyols. The general gist of the rejection is that while Gunatillake does not specifically show manufacture

of polytrimethylene ether glycol as claimed, the general teachings pertain to making this class of polyol and therefore without unexpected results the claimed invention is not patentable.

Gunatillake disclosed a process for the polymerization of polyhydroxy compounds, including alkanediols having from 2-20 carbon atoms, in the presence of an acid resin catalyst at temperatures of from 130-220°C. Molecular weights of from 150 to 10,000 are mentioned. Gunatillake is primarily focused on use of larger diols as starting materials, as can be seen at column 3, lines 38-46. Note that all of the examples are directed to larger diols of (i.e., 1,6-hexanediol, 1,8-octanediol or 1,10-decanediol), and Example 9 is using 1,3-propanediol as a secondary starting material.

A copolymer of 1,10-decanediol and 1,3-propanediol was prepared in Example 9 of Gunatillake. A low temperature process is not used. Example 9 shows equal molar amounts of 1,10-decanediol and 1,3-propanediol.

Claims 1 and 39 are directed to a process of preparing PO3G. They specify that 20 weight % or less of comonomer diol is used.

Gunatillake contains general teachings concerning forming polyols, but it is not focused on polytrimethylene ether glycols. Instead, Gunatillake is primarily focused on condensing larger diols into polyols. In this regard, all of the examples use at least 50 mole % of 1,6-hexanediol, 1,8-octanediol or 1,10-decanediol. Example 9 uses 50 mole % 1,3-propandiol as a co-monomer.

The reason Gunatillake focuses on the higher diols as starting materials is that it is well known that short chain diols, such as ethylene glycol and butanediol, can not be reacted to form linear polyols, whereas the larger diols were known to be useful for forming linear polyols.

Concerning this point, it is well known to a person of ordinary skill in the art that ethylene glycol cannot be polymerized to a homopolymer in the presence of an acid catalyst because the ethylene glycol dimerizes first to diethylene glycol, and subsequently the diethylene glycol cyclizes to 1,4-dioxane. Applicants direct the Examiner's attention to pages 695-700 of the Encyclopedia of Chemical Technology, Kirk-Othmer, Vol. 12, 4th Ed., John Wiley & Sons, Inc. (1994), which is enclosed herewith. More specifically, applicants direct the Examiner's attention to page 699, wherein Exhibit A expressly indicates that "[d]iethylene glycol readily dehydrates using an acid catalyst to make 1,4-dioxane", and that "[e]thylene glycol also produces 1,4-dioxane by acid-catalyzed dehydration to diethylene glycol followed by cyclization." As evidenced by this article, applicants respectfully assert that a person of ordinary skill in the art would know that an ethylene glycol cannot be polymerized to a

homopolymer in the presence of an acid catalyst, but rather forms a diethylene glycol and then cyclizes to 1,4-dioxane in the presence of an acid catalyst.

Likewise, it is well known to the person of ordinary skill in the art that butane diol forms tetrahydrofuran (THF) under acidic conditions. See, S.H. Vaidy et al., "Reaction kinetics studies on catalytic dehydration of 1,4-butanediol using cation exchange resin", Applied Catalysis A: General, 242, pp. 321-328 (2003), enclosed herewith.

Given the above, the person of ordinary skill in the art would not consider the lower diols to make linear polyether glycols. Therefore, Gunatillake does not teach or suggest the claimed processes.

Applicants also submit that Gunatillake does not teach or suggest the claimed polytrimethylene ether glycols. Claim 44 is directed to a polytrimethylene ether glycol produced by the process of claim 1, having a number average molecular weight of greater than 1,500 and a dispersity of 1.5 to 2.1. Claim 46 is directed to polytrimethylene ether glycol having a number average molecular weight greater than 1,500, an APHA color of less than 120, an unsaturation of less than 20 meq/kg, and a content of cyclic ether oligomers of less than 2%. Claim 59 is directed to polytrimethylene ether glycol produced by the process of claim 1, having a number average molecular weight greater than 1,500, an APHA color of less than 120, an unsaturation of less than 15 meq/kg, and a dispersity of 1.5 to 2.1. Claim 60 is directed to polytrimethylene ether glycol having a number average molecular weight greater than 1,500, an APHA color of less than 120, and an unsaturation of less than 15 meq/kg.

First, it is noted that Gunatillake does not teach or suggest a polytrimethylene ether glycol having the properties of any of the polytrimethylene ether glycol claims.

Second, Gunatillake can not be read in isolation. Gunatillake must be read in view of the art, considering making polytrimethylene ether glycol from 1,3-propanediol reactant, including the teachings of Mason.

In considering the state of the art concerning polytrimethylene ether glycol from 1,3-propanediol reactant one can see that U.S. Patent No. 2,520,733 Morris et al discloses that the trimethylene glycol derived polymers disclosed in this patent are dark brown or black in color. At best, the color can be improved to a light yellow color by treatment processes disclosed therein.

Mason teaches preparing polytrimethylene glycol which has an average molecular weight of about 900 followed by an after treatment which comprises vacuum stripping the polyglycol at a temperature in the range of 220-240°C and at a pressure of 1-8 mm Hg in a current of

nitrogen from 1-6 hours. There is nothing in Gunatillake that would lead the person of ordinary skill in the art to believe that polytrimethylene glycol having better properties than those described in Mason or Morris can be prepared using the process of Gunatillake. This is particularly true since Gunatillake is focused on making polyols from higher polyols and doesn't teach anything with respect to improving the process for making polytrimethylene glycol.

Third, applicants point out that the polymer prepared in Example 9 of Gunatillake had a molecular weight of 930 when measured by NMR, whereas the polytrimethylene glycol of the claims has a higher number average molecular weight when measured by NMR, and also the dispersity of the polymer of Gunatillake's Example 9 is outside the claimed dispersity.

Given the above, the person of ordinary skill in the art would not consider Gunatillake to teach or suggest the claimed polytrimethylene glycols.

For the above reasons, Gunatillake doesn't teach or suggest the claimed inventions, and withdrawal of the rejection under 35 USC 103(a) over Gunatillake is respectfully requested.

Amendments

Because the specification included a blank line, the amendments are presented using double underlining to show insertions.

Support for the amendments is as follows.

Page 7 of the specification is amended to show the patent application number and patent number of the corresponding patent application having applicant's docket number CL1483.

Pages 8-9 are amended to list the patents issued based on the cited patent applications.

Claims 1 is amended to recite that the optional comonomer diols are present in an amount of 20 weight % or less as supported at page 9, lines 13-27. Claim 1 is also clarified by reciting that the polycondensation is carried out using the catalyst.

Claims 31, 32, 46 and 49 are amended to recite that the percentage is a weight percentage as supported in Table 2 at page 13 ("OCE wt%).

Claim 33 is redrafted in independent form. It recites the 1-20 mole % comonomer range supported at page 4, lines 26-32.

Claims 36 and 37 have been amended as discussed above

Claims 39 is amended to recite that the optional comonomer diols are present in an amount of 20 weight % or less as supported at page 9, lines 13-27. Claim 39 is also amended as described above with respect to 35 USC 112 and to refer to the catalyst in steps b and c for clarity.

Claim 44 is amended to recite that the polytrimethylene ether glycol has a number average molecular weight of greater than 1,500 and a dispersity of 1.5 to 2.1 as supported at page 4, lines 10-14, etc.

Claim 44 is amended to recite that the polytrimethylene ether glycol has a dispersity of 1.5 to 2.1 as supported at page 4, lines 13-14.

Claims 50-52 and 66-68 are supported at page 9, lines 17-26.

Claims 53 and 69 are supported at page 3, lines 10-15, page 4, lines 26-33, etc.

Claims 54 and 70 are supported at page 10, lines 1-21, and page 4, lines 7-9, 14-15, 19-21 and 24-25.

Claims 55 and 71 are supported at page 4, lines 7-9.

Claims 56 and 72 are supported at page 10, lines 4-11.

Claims 57-60 are supported at page 4, lines 10-12 and in original claims 16, 17 and 20.

Claim 73 is supported at page 4, lines 16-21.

Claim 74 is supported in claim 39 and at page 4, lines 26-33.

Claim 75-78 are based upon claim 40, 34, 35 and 38, respectively. Claims 76-77 also find support at page 4, lines 26-34.

Claim 79 finds support at page 6, lines 5-7, page 10, lines 15, 23 and 25, and in claim 44.

Claims 80 and 81 are the same as amended claims 44 and 45, respectively, but depends on claim 39.

Claim 82 is supported at page 4, line 19.

Claims 83-85 are based upon claims 47-49, respectively.

Claims 86 and 87 are the same as claim 44, but depend on claims 33 and 74.

Entry and consideration are respectfully requested.

Conclusions

In view of the foregoing, allowance of the above-referenced application is respectfully requested. Should there remain any matters unresolved by this response, the Examiner is invited to telephone the undersigned at the below-listed telephone number.

Respectfully submitted,



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GLYCOLS

CL-1482

Ethylene glycol and oligomers, 695

Propylene glycols, 715

Other glycols, 726

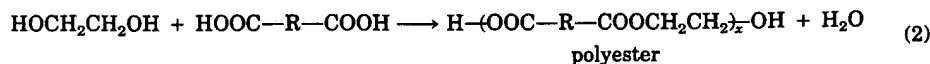
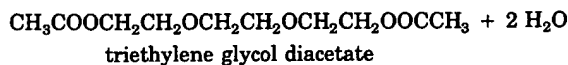
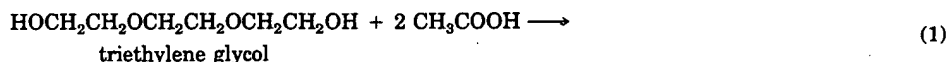
ETHYLENE GLYCOL AND OLIGOMERS

Glycols are diols, compounds containing two hydroxyl groups attached to separate carbon atoms in an aliphatic chain. Although glycols may contain heteroatoms, those discussed here are composed solely of carbon, hydrogen, and oxygen. These are adducts of ethylene oxide and can be represented by the general formula, $C_{2n}H_{4n}O_{n-1}(OH)_2$.

Ethylene glycol, the adduct of water and ethylene oxide, is the simplest glycol and is the principal topic of this article. Diethylene, triethylene, and tetraethylene glycols are oligomers of ethylene glycol. Polyglycols are higher molecular weight adducts of ethylene oxide and are distinguished by intervening ether linkages in the hydrocarbon chain. These polyglycols are commercially important; their properties are significantly affected by molecular weight. They are water soluble, hygroscopic, and undergo reactions common to the lower weight glycols (see also POLYETHERS, ETHYLENE OXIDE POLYMERS).

Ethylene glycol, EG, is a colorless, practically odorless, low viscosity, hygroscopic liquid of low volatility. It is completely miscible with water and many organic liquids. EG was first prepared by Wurtz in 1859 by hydrolysis of ethylene glycol diacetate. It did not achieve commercial interest until World War I, when it was used in Germany as a substitute for glycerol (qv) in explosives manufacture (1). The uses for ethylene glycol are numerous. Some of the applications are polyester resins for fiber, PET containers, and film applications; all-weather automotive antifreeze and coolants, defrosting and deicing aircraft; heat-transfer solutions for coolants for gas compressors, heating, ventilating, and air-conditioning systems; water-based formulations such as adhesives, latex paints, and asphalt emulsions; manufacture of capacitors; and unsaturated polyester resins. The oligomers also have excellent water solubility but are less hygroscopic and have somewhat different solvent properties. The number of repeating ether linkages controls the influence of the hydroxyl groups on the physical properties of a particular glycol.

Glycols undergo reactions common to monohydric alcohols forming esters, acetals, ethers, and similar products. For example, both simple and polyesters are produced by reaction with mono- or dibasic acids (eqs. 1 and 2):



Physical Properties

Ethylene glycol and its lower polyglycols are colorless, odorless, high boiling, hygroscopic liquids completely miscible with water and many organic liquids. Physical properties of ethylene glycols are listed in Table 1. Vapor-pressure curves of the ethylene glycols at various temperatures are illustrated in Figure 1. Ethylene glycols markedly reduce the freezing point of water (Fig. 2). Some important physical constants of ethylene glycol are given in Table 2.

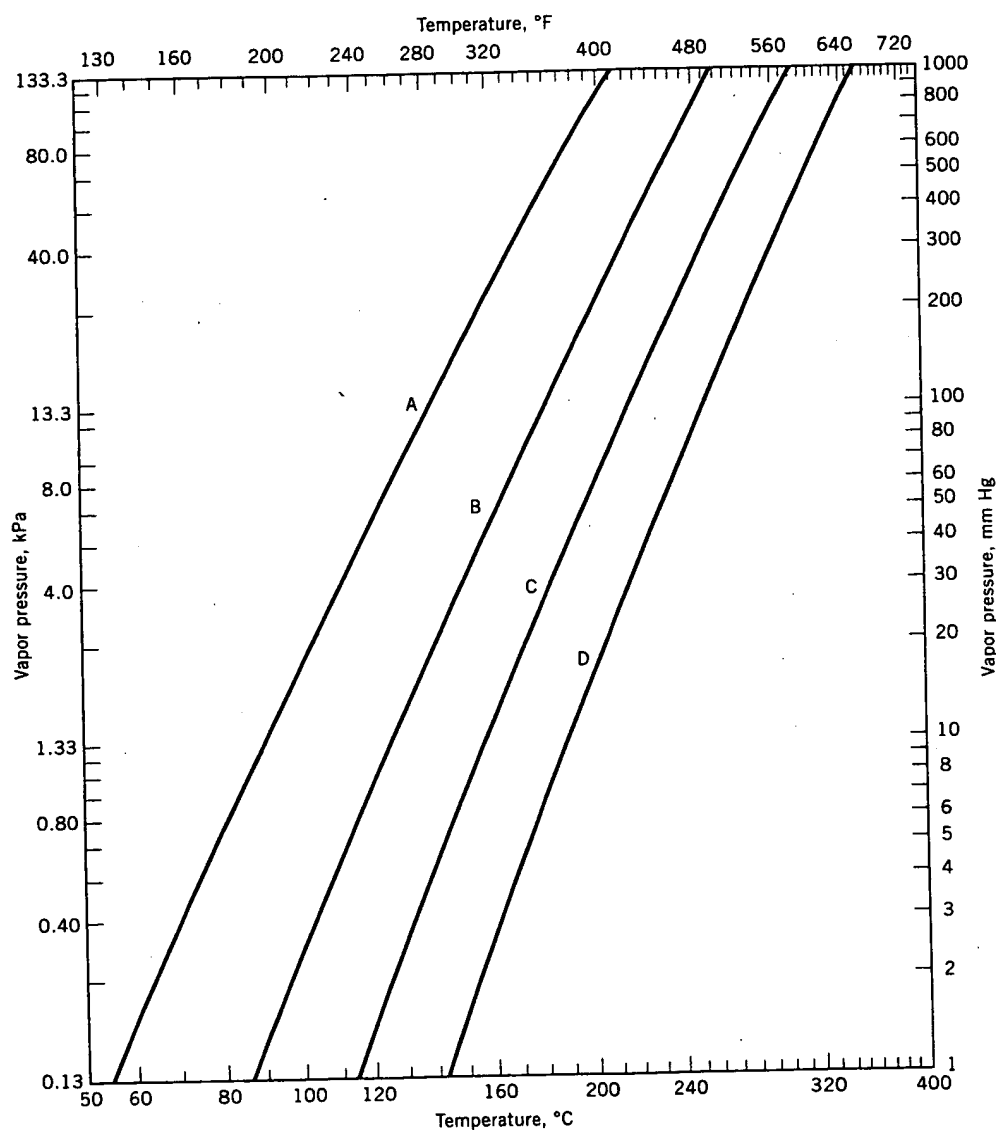


Fig. 1. Vapor pressures of glycols at various temperatures. A, ethylene glycol; B, diethylene glycol; C, triethylene glycol; and D, tetraethylene glycol.

Table 1. Properties of Glycols^a

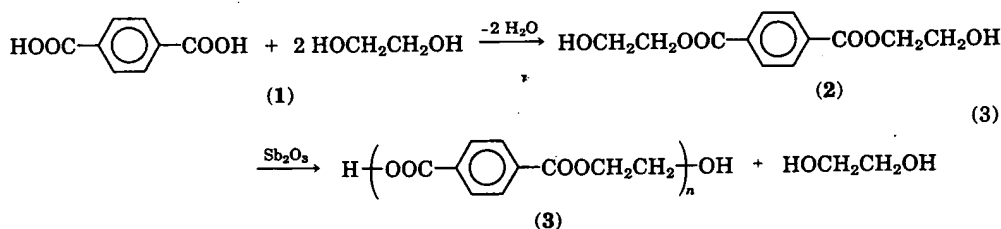
Property	Ethylene glycol	Diethylene glycol	Triethylene glycol	Tetraethylene glycol
CAS Registry Number	[107-21-1]	[111-46-6]	[112-27-6]	[112-60-7]
formula	HOCH ₂ CH ₂ OH	HO(CH ₂ CH ₂ O) ₂ H	HO(CH ₂ CH ₂ O) ₃ H	HO(CH ₂ CH ₂ O) ₄ H
mol wt	62.07	106.12	150.17	194.23
sp gr, 20/20°C	1.1155	1.1185	1.1255	1.1247
bp at 101.3 kPa, ^b °C	197.6	245.8	288	dec
mp, °C	-13.0	-6.5	-4.3	-4.1
viscosity at 20°C, mPa·s (= cP)	20.9	36	49	61.9
refractive index, n _D ²⁰	1.4318	1.4475	1.4561	1.4598
heat of vaporization at 101.3 kPa, ^b kJ/mol ^c	52.24	52.26	61.04	62.63
flash point of commercial material, °C	116 ^d	138 ^e	172 ^e	191 ^e

^aRef. 2-5.^bTo convert kPa to mm Hg, multiply by 7.5.^cTo convert kJ to kcal, divide by 4.184.^dDetermined by ASTM D56, using the Tag closed cup.^eDetermined by ASTM D92, using the Pensky-Martens closed cup.

Chemical Properties

The hydroxyl groups on glycols undergo the usual alcohol chemistry giving a wide variety of possible derivatives. Hydroxyls can be converted to aldehydes, alkyl halides, amides, amines, azides, carboxylic acids, ethers, mercaptans, nitrate esters, nitriles, nitrite esters, organic esters, peroxides, phosphate esters, and sulfate esters (6,7).

The largest commercial use of ethylene glycol is its reaction with dicarboxylic acids to form linear polyesters. Poly(ethylene terephthalate) [25038-59-9] (PET) is produced by esterification of terephthalic acid [100-21-0] (1) to form bishydroxyethyl terephthalate [959-26-2] (BHET) (2). BHET polymerizes in a transesterification reaction catalyzed by antimony oxide to form PET (3).



Ethylene glycol esterification of BHET is driven to completion by heating and removal of the water formed. PET is also formed using the same chemistry start-

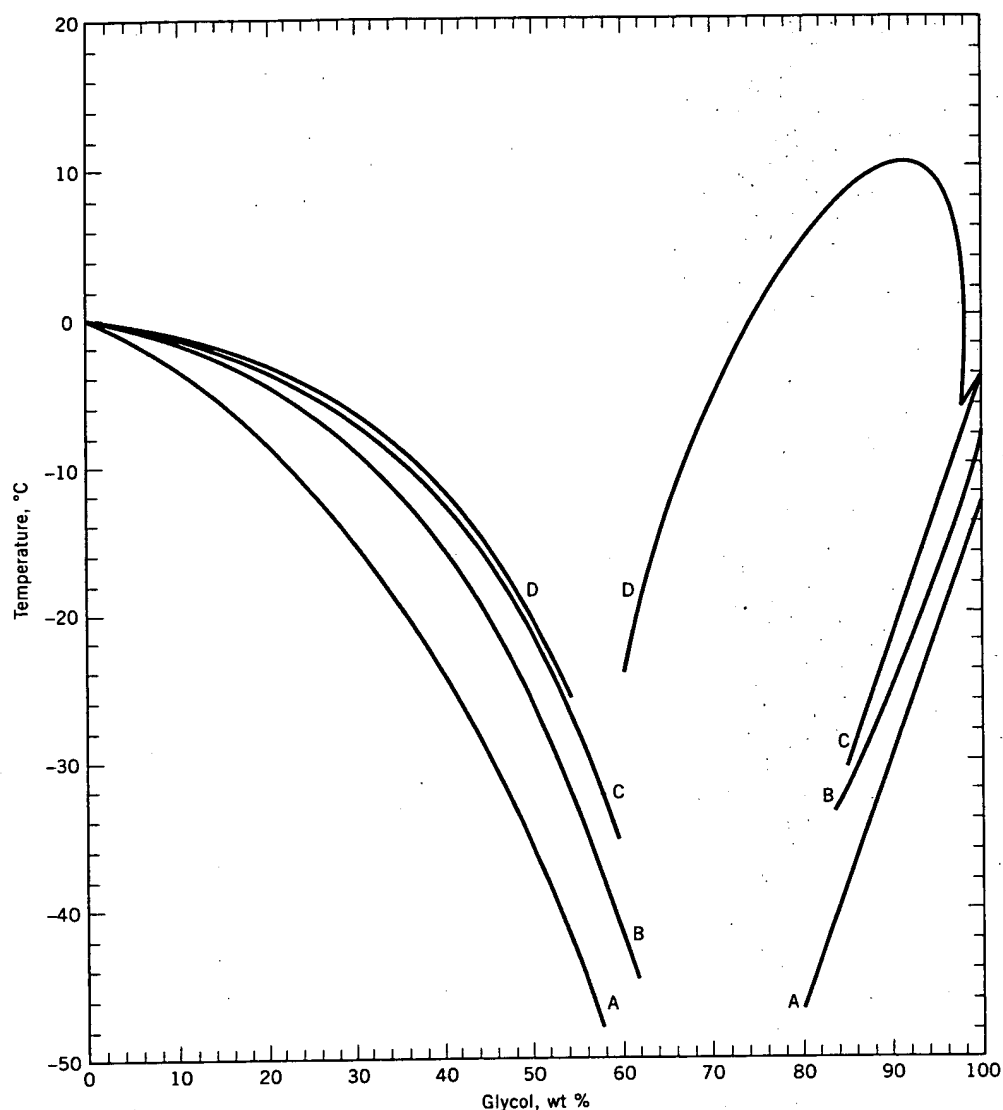


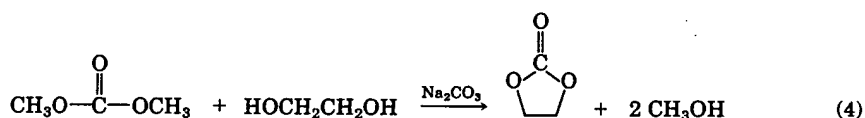
Fig. 2. Freezing points of aqueous glycol solutions. A, ethylene glycol; B, diethylene glycol; C, triethylene glycol; and D, tetraethylene glycol. Ethylene glycols form a slush with water in the apparent discontinuous ranges.

ing with dimethyl terephthalate [120-61-6] and ethylene glycol to form BHET also using an antimony oxide catalyst.

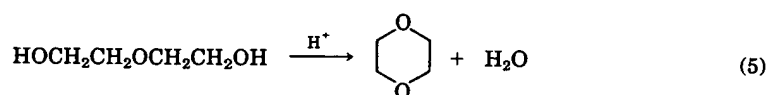
Glycols may undergo intramolecular cyclization or cyclically condense with other molecules to form a number of ring structures. Transesterification of carbonates with ethylene glycol produces ethylene carbonate [96-49-1] (eq. 4). Numerous materials catalyze carbonate transesterifications.

Table 2. Physical Properties of Ethylene Glycol^a

Property	Value
flash point	
Pensky-Martens closed cup, °C	127
Cleveland open cup, °C	127
autoignition temperature, °C	400
density at 20°C, g/mL	1.1135
surface tension at 20°C, mN/m(= dyn/cm)	48.4
specific heat, J/(g·K) ^b	
as liquid, 19.8°C	2.406
as ideal gas, 25°C	1.565
electrical conductivity at 20°C, S/m	1.07×10^{-4}
solubility in water at 20°C, % by wt	100.0
solubility of water in EG at 20°C, % by wt	100.0
heat of combustion at 25°C, kJ/mol ^b	-1189.595
heat of formation at 25°C, kJ/mol ^b	-392.878
heat of fusion, kJ/mol ^b	11.63
onset of initial decomposition, °C	165
critical constants	
temperature, °C	446.55
pressure, kPa ^c	6515.73
volume, L/mol	0.186
compression factor, Z_c	0.2671
viscosity, mPa·s(= cP)	
at 0°C	51.37
at 40°C	9.20

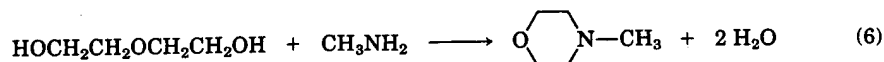
^aRef. 2; see also Table 1.^bTo convert J to cal, divide by 4.184.^cTo convert kPa to mm Hg, multiply by 7.5.

Diethylene glycol readily dehydrates using an acid catalyst to make 1,4-dioxane [123-91-1] (eq. 5).

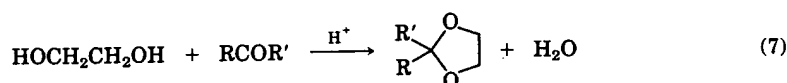


Ethylene glycol also produces 1,4-dioxane by acid-catalyzed dehydration to diethylene glycol followed by cyclization. Cleavage of triethylene and higher glycols with strong acids also produces 1,4-dioxane by catalyzed ether hydrolysis with subsequent cyclization of the diethylene glycol fragment. Diethylene glycol con-

denses with primary amines to form cyclic structures (eq. 6), eg, methylamine [74-89-5] reacts with diethylene glycol to produce *N*-methylmorpholine [109-02-4].



Ketones and aldehydes react with ethylene glycol under acidic conditions to form 1,3-dioxolanes (cyclic ketals and acetals) (eq. 7).

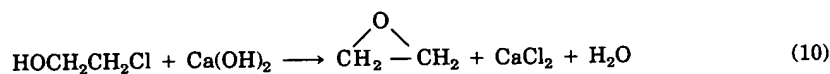
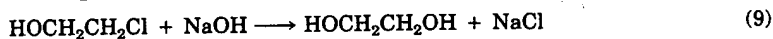
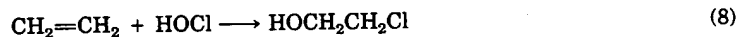


Manufacture

In 1937 the first commercial application of the Lefort direct ethylene oxidation to ethylene oxide [75-21-8] followed by hydrolysis of ethylene oxide became, and remains in the 1990s, the main commercial source of ethylene glycol production (1) (see ETHYLENE OXIDE). Ethylene oxide hydrolysis proceeds with either acid or base catalysis or uncatalyzed in neutral medium. Acid-catalyzed hydrolysis activates the ethylene oxide by protonation for the reaction with water. Base-catalyzed hydrolysis results in considerably lower selectivity to ethylene glycol. The yield of higher glycol products is substantially increased since anions of the first reaction products effectively compete with hydroxide ion for ethylene oxide. Neutral hydrolysis (pH 6–10), conducted in the presence of a large excess of water at high temperatures and pressures, increases the selectivity of ethylene glycol to 89–91%. In all these ethylene oxide hydrolysis processes the principal by-product is diethylene glycol. The higher glycols, ie, triethylene and tetraethylene glycols, account for the remainder.

The large excess of water from the hydrolysis is removed in a series of multiple-effect evaporators (8), and the ethylene glycol is refined by vacuum distillation. Figure 3 depicts a typical process flow diagram.

Ethylene glycol was originally commercially produced in the United States from ethylene chlorohydrin [107-07-3], which was manufactured from ethylene and hypochlorous acid (eq. 8) (see CHLOROHYDRINS). Chlorohydrin can be converted directly to ethylene glycol by hydrolysis with a base, generally caustic or caustic/bicarbonate mix (eq. 9). An alternative production method is converting chlorohydrin to ethylene oxide (eq. 10) with subsequent hydrolysis (eq. 11).





Reaction kinetics studies on catalytic dehydration of 1,4-butanediol using cation exchange resin

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Abstract

In the present work, we report kinetics of dehydration of 1,4-butanediol to tetrahydrofuran (THF) using a strong acid cation exchange resin as catalyst. Effects of various parameters such as temperature, catalyst concentration, substrate concentration, initial water concentration, speed of agitation and also effect of solvent have been investigated in detail. The initial rate varies linearly with reaction temperature. Also, we observed a strong dependence of rate on catalyst loading; this also followed a linear relationship. The rate data showed exponential dependence on initial substrate concentration. Water was found to inhibit the reaction due to the strong adsorption of water on active acid sites of resin. A mechanism has been proposed to explain the reaction behaviour. Contributions of film diffusion and intraparticle diffusion were found to be negligible in the range of parameters studied in this work. Reactor performance under integral conditions was predicted successfully using the proposed rate model.

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Keywords: Dehydration; Kinetics; 1,4-Butanediol; Catalyst; Ion exchange resin

1. Introduction

Dehydration of 1,4-butanediol to tetrahydrofuran (THF) is an important reaction step involved in the manufacturing of THF, in the processes starting from both acetylene and maleic anhydride. Both processes are industrially established. Dehydration of 1,4-butanediol is catalysed by liquid or solid acids such as mineral acids, heteropoly acids, silica gel, alumina and cation exchange resins. Although the use of cation exchange resins is well known in the dehydration of alcohols [1–3], the kinetics of dehydration of 1,4-butanediol using strong acid cation exchange

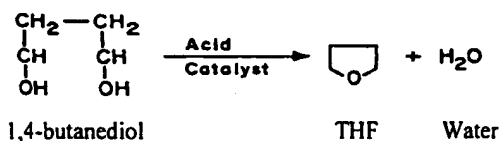
resins has not been reported in the literature. Toshihide and Yoshio [4] have reported kinetics of liquid phase dehydration of 1,4-butanediol to THF in the presence of heteropoly acid as catalyst. Li et al. [5] have reported use of active terra alba supported $H_3PW_{12}O_{40}$ catalyst for gas–solid reaction. A number of patents also report use of such catalysts and vapour phase reaction for improved conversion levels. The use of a cation exchange resin as catalyst has distinct advantages over liquid catalysts such as mineral acids. The main advantages are no corrosion problems, ease of handling and ease of separation of catalyst. Apart from these process engineering aspects, the resins as catalysts also offer higher local concentration of H^+ ions and thereby higher catalytic activity, fewer side reactions and mild operating conditions of temperature and pressure.

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Since few articles describe dehydration of 1,4-butanediol to THF in general, and with catalyst involving cation exchange resin, in particular, it would be instructive to study the application of strong acid cation exchange resin as catalyst for this reaction. The present study investigates kinetics of dehydration of 1,4-butanediol using a strongly acidic cation exchange resin, Indion-130. Effects of various kinetic parameters such as catalyst concentration, temperature, substrate concentration and water on the initial rate of the reaction have been studied. A suitable rate model has also been proposed and applicability of this model under integral conditions has been proved by predicting batch reactor performance using the model and matching the results with experimental data.

2. Experimental

Dehydration of 1,4-butanediol in the presence of acid catalyst to give THF can be represented as



In this reaction, cyclization of 1,4-butanediol takes place by elimination of water.

The experiments were carried out in a 300 ml Parr autoclave equipped with a variable speed magnetic stirrer, cooling coil and PID controller (supplied by Parr Instruments Co., USA). The experimental set-up is shown in Fig. 1. A strong acid cation exchange resin, Indion-130 in H⁺ form (supplied by Ion Exchange (I) Ltd.) was used as a catalyst. The characterisation of the resin was carried out as per the standard procedures [6]; characteristics of the resin are given in Table 1. 1,4-Butanediol, supplied by Fluka, was chemically pure with minimum assay of 99%. The solvent, 1,4-dioxane (CP Grade with minimum 99% assay) was supplied by SD Fine Chem., India. All other chemicals and reagents used in the study were AR grade and were supplied by companies of repute.

The experiments were carried out by charging in the reactor a known quantity of 1,4-butanediol in solvent along with a predetermined quantity of the catalyst. The reactor was then flushed with nitrogen several

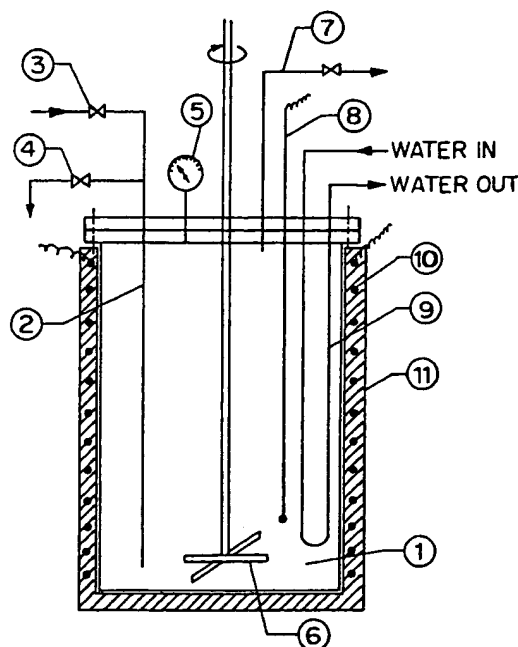


Fig. 1. Schematic of batch reactor set-up: 1, pressure bomb; 2, dip tube; 3, gas inlet valve; 4, sampling valve; 5, pressure indicator; 6, stirrer; 7, gas vent; 8, thermocouple; 9, cooling coil; 10, reactor heating; 11, insulation.

times. The reaction was started by bringing the reaction mass to the desired temperature and starting agitation. The reactant, 1,4-butanediol has a boiling point of 230 °C, significantly higher than the reaction temperature. After charging the reaction mass to the reactor and bringing the temperature of the mass to the desired reaction temperature, a pressure rise of about 1 kg/cm² was observed, this did not significantly change during the course of reaction as the conversion of 1,4-butanediol was far from being complete. The reaction is essentially a liquid phase reaction with the

Table 1
Characteristics of Indion-130

Resin	Macroporous, strong acid
DVB content (%)	14
Porosity (cc/g)	0.33
Average pore diameter (Å)	300
Particle size (m)	0.3–1.2 × 10 ^{−3}
Bulk density (kg/m ³)	0.55 × 10 ^{−3}
Exchange capacity (meq/g)	4.8
Temperature stability (K)	423

Table 2
Range of reaction parameters

Parameter	Range
Temperature (K)	353–398
Catalyst concentration (kg/m ³)	10–40
Substrate concentration (kmol/m ³)	1.67–6.7
Initial water concentration (kmol/m ³)	2.77–22.2
Agitation speed (Hz)	1.66–13.3

solid catalyst suspended uniformly in the liquid reaction medium. Each initial sample was withdrawn at zero time (time at which the reaction mass reaches the reaction temperature and agitation starts) and analysed for 1,4-butanediol. Thereafter, liquid samples were withdrawn at regular intervals and were analysed for 1,4-butanediol consumed. The analysis of the liquid samples was carried out using a chromosorb-101 column and a FID detector on a DANI gas chromatograph coupled with a Spectraphysic integrator. Water in the reaction mixture was analysed using the Karl–Fischer method [7]. We ensured that the total quantity of samples removed represent only a fraction of the total reaction mass and hence does not contribute significantly to changes in the volume of reaction mass. The material balance was found satisfactory; the error in the analysis was in the range of 3–5%. The experimental parameters and their ranges are given in Table 2.

3. Results and discussion

The use of ion exchange resins as catalysts represents a promising alternative to conventional liquid acid catalysts in a variety of reactions, especially when the reaction conditions are mild. Strongly acidic resins have been most commonly used for this purpose. Although the distinction between the use of liquid acid catalysts such as sulphuric acid and solid acid catalyst such as ion exchanger is fairly well understood for many reactions, a more detailed study is required on the comparison/a priori selection of solid acid catalysts. In the present study, preliminary experiments were carried out using Indion-130, silica gel and alumina. The results have indicated high activity for Indion-130 (Fig. 2). Since the resin catalyst exhibits much higher activity at much lower reaction temperature, its application to this industrially

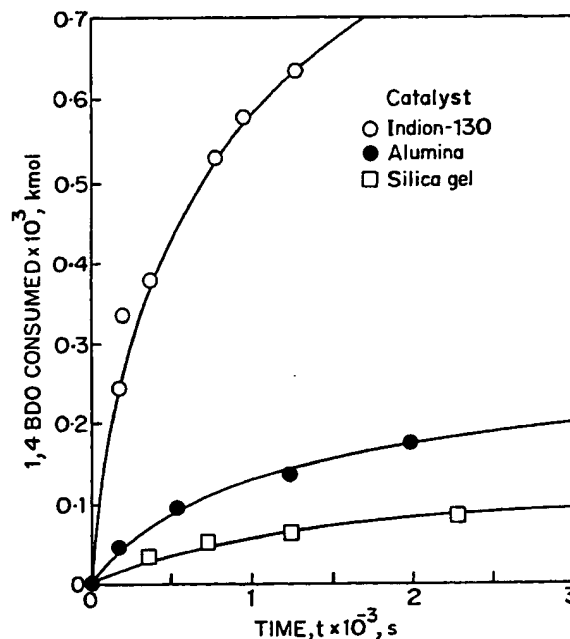


Fig. 2. Effect of catalyst type. Catalyst loading: 30 kg/m³; temperature: Indion-130 (398 K), alumina (505 K), silica gel (498 K).

important reaction would be useful and therefore was studied in detail.

Before studying intrinsic kinetics, it is essential to assess the influence of mass transfer resistances under reaction conditions and one must collect rate data in the kinetic regime. Liquid–solid external mass transfer resistance influence can be evaluated from the effect of agitation speed on the initial rate. Beyond the agitation speed of 10.33 Hz, there is no change in the initial rate of reaction, indicating that liquid–solid mass transfer resistance has no effect above this speed of agitation. Therefore, kinetic data was collected using agitation speed above this value. The importance of intraparticle diffusion can be assessed by the Thiele parameter and effectiveness factors calculated using the method given by Satterfield [8]. The Thiele modulus is defined as

$$\phi = \frac{R^2}{D_e} \left[-\frac{1}{v} \frac{dn_A}{dt} \right] \frac{1}{C_{As}} \quad (1)$$

where R is the average radius of catalyst particle (m), n_A the number of moles of A (kmol), C_A the concentration (kmol/m³) while subscript “s” denotes the surface concentration, D_e the effective diffusivity (m²/s) and the term $((1/v)(dn_A/dt))$ is the rate

of reaction based on volume ($\text{kmol/m}^3 \text{ s}$). For obtaining the Thiele modulus, the value of the effective diffusivity was calculated using the following equation:

$$D_e = 19400 \frac{\theta^2}{\tau S_g \rho_p} \sqrt{\frac{T}{M}} \quad (2)$$

where θ is the porosity, τ the tortuosity factor, S_g the specific surface area (m^2/g), T the reaction temperature (K), M the molecular weight of reactant and ρ_p is the particle density (kg/m^3).

A tortuosity factor value of 3 was used for the resin. Using the highest observed reaction rate, the value of the Thiele modulus was found to be 0.0162. From the graph of η versus ϕ for the first order reaction, the effectiveness factor for this value of Thiele modulus was very close to unity. Thus, the results indicate that influence of intraparticle diffusion is practically negligible. This also confirms that the data fall in the kinetic regime.

3.1. Effect of substrate concentration

The effect of 1,4-butanediol concentration on the rate of reaction was studied in the concentration range of 1.66–6.67 kmol/m^3 for four temperatures, viz. 353, 368, 383 and 398 K. A fixed catalyst loading of 20 kg/m^3 was used in these studies. The results of these studies are presented in Fig. 3 in the form of initial reaction rate versus substrate concentration at different temperatures. The results indicate first order dependence with respect to 1,4-butanediol.

3.2. Effect of catalyst concentration

The effect of catalyst loading was studied at different temperatures in the same range as mentioned above. The results of the study are shown in Fig. 4. Here, the initial rate was found to vary linearly with catalyst concentration.

3.3. Effect of solvent

Since the solvent is known to alter the reaction rate by way of interaction with the solute in the form of hydrogen bonding, dipole interaction, etc. it is instructive to study the effect of solvent in the present reaction

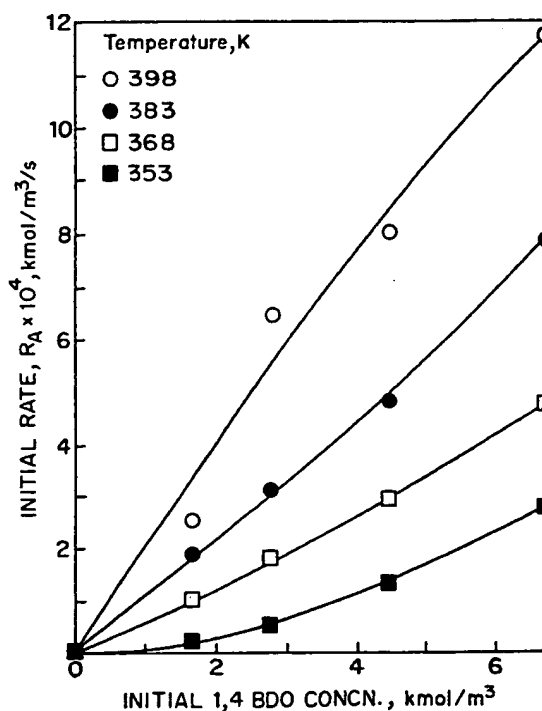


Fig. 3. Effect of 1,4-butanediol concentration on initial rate (catalyst loading: 20 kg/m^3).

system. However, in the present study, the objective is not to make detailed analysis on the effect of different solvents, but to present effect of the solvent on reaction, if any, and to make a qualitative comparison of various solvents.

The effect of solvent was studied at 398 K using 5% (w/v) catalyst loading. The solvents used were ethanol, 1,4-dioxane and water. The reactants and products were completely miscible in these solvents. The results of the study are presented in Fig. 5. With 1,4-dioxane as solvent, the reactivity is higher than with the other two solvents. Water was found to give the lowest activity as expected. Lower reactivity in solvents like ethanol and water can be attributed to the possibility of competitive adsorption of $-\text{OH}$ groups of these solvents on the active sites with $-\text{OH}$ groups of 1,4-butanediol [1].

3.4. Effect of initial water concentration

As the water inhibits the reaction, the effect of initial water concentration was studied separately.

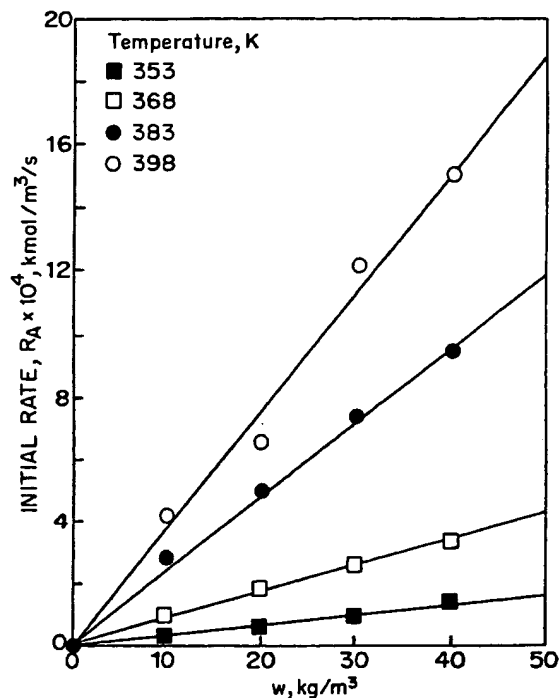


Fig. 4. Effect of catalyst loading (1,4-butanediol concentration: 2.77 kmol/m³).

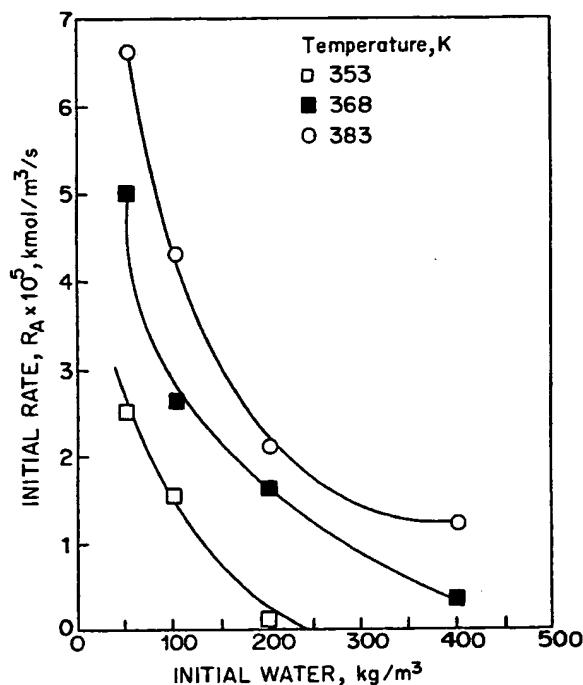


Fig. 6. Effect of initial water concentration. 1,4-Butanediol concentration: 2.77 kmol/m³; catalyst loading: 20 kg/m³.

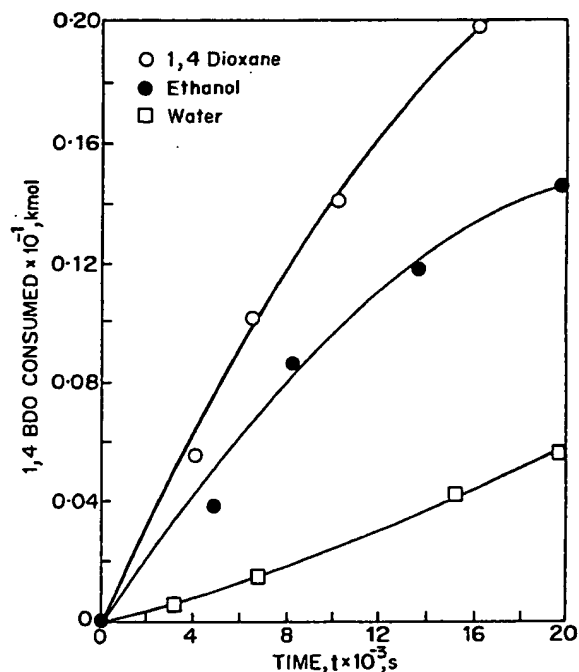


Fig. 5. Effect of solvent. Temperature: 383 K; 1,4-butanediol concentration: 2 kmol/m³.

These experiments were carried out by adding a known quantity of water in the beginning of the experiment. The range of water concentration for the study was 2.77–22.2 kmol/m³. The effect was also studied at different temperatures. The results of the initial water effect are shown in Fig. 6 in the form of initial rate versus water concentration. The reaction rates were found to decrease significantly with increase in the initial water concentration at all the temperatures. This clearly substantiates that strong inhibition due to water occurs. The strong inhibition effect can be explained on the basis of adsorption of water on the active ion exchange sites, as indicated in Fig. 7. Water has a strong affinity for the $-\text{SO}_3\text{H}$ groups; due to its strong adsorption, the number of sites available for chemisorption of 1,4-butanediol are substantially reduced, which consequently affects the rate of reaction [1,2]. Also, in the presence of water, polarity of the medium increases, facilitating solvation of the ionic groups and thereby reducing the concentration of pedant groups on the resin surface [9].

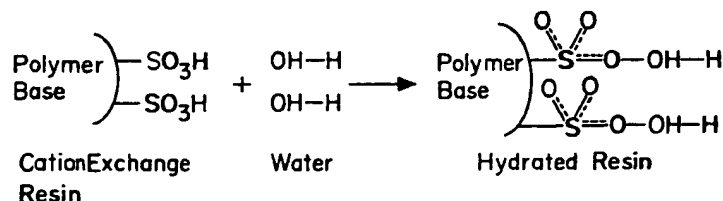


Fig. 7. Reaction inhibition mechanism.

4. Reaction mechanism

Gates and Jonson [10] have proposed a reaction mechanism for dehydration of methyl alcohol using cation exchange resin as catalyst. The mechanism suggests an intermediate complex formation through the strong chemisorption of methanol molecules on $-\text{SO}_3\text{H}$ sites. Using this approach, we propose the following reaction mechanism for the dehydration of 1,4-butanediol.

The proposed reaction mechanism is shown in Fig. 8. The reaction can be assumed to follow a two-step process: (1) adsorption of 1,4-butanediol on the adjacent sulfonic groups of the resin, resulting into formation of an intermediate; (2) decomposition of the intermediate complex to give THF and water. Such a dual site sorption mechanism is plausible in view of high surface charge density of these resins

[11,12]. As discussed earlier, the resulting water can also compete in the adsorption process. Therefore, a more detailed analysis of the mechanism incorporating adsorption/desorption steps for various reactants and products needs to be done.

5. Kinetic model and fit to the experimental data

The rate data obtained in the kinetic regime was fitted using various Langmuir–Hinshelwood type models with a product-inhibition term. The following rate equation was found to satisfactorily explain the rate behaviour:

$$R_A = \frac{k_w K_A C_A^2}{1 + K_A C_A + K_w C_w} \quad (3)$$

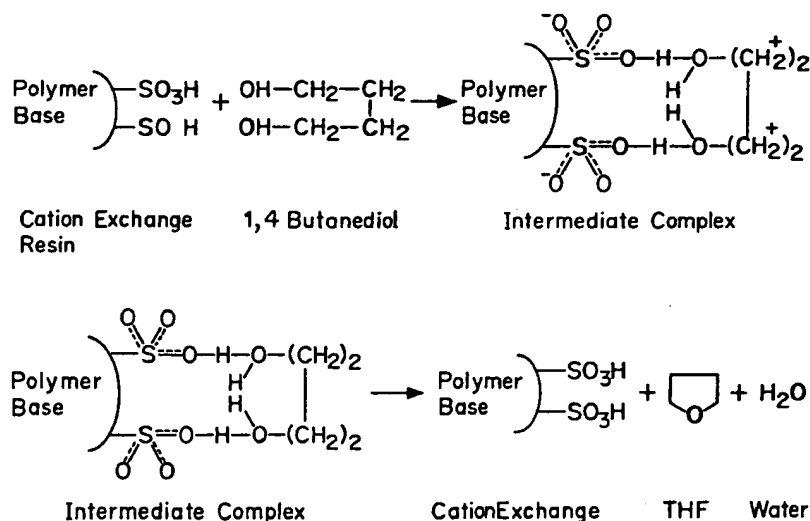


Fig. 8. Proposed dual site sorption mechanism.

Table 3
Values of constants in Eq. (3)

Temperature (K)	$k \times 10^{-3}$ (m ³ /kg s)	$K_A \times 10^{-3}$ (m ³ /kmol)	$K_W \times 10^{-3}$ (m ³ /kmol)
353	0.00568	91.30	737
368	0.00710	250.3	140
383	0.00902	1660	958

Here k is the reaction rate constant (m³/kg s), C_w the initial water concentration (kmol/m³), w the catalyst concentration (kg/m³), and K_A and K_W are the adsorption equilibrium constants for substrate and water (m³/kmol), respectively. The values of various constants in Eq. (3) are given in Table 3. Fit of the rate model under various reaction conditions is illustrated in Table 4 using the initial rate data. It is evident that the fit of the rate model is good in the range of experimental parameters of this work. Although the values of the rate constant increase with temperature as expected, the values of the adsorption equilibrium constants have not showed clear decreasing trend with increase in the temperature. This may be due to the complexities involved in the surface phenomenon due to multicomponent adsorption/desorption/ionic interactions, as indicated in the reaction mechanism.

The activation energy calculated from the Arrhenius plot (Fig. 9) was found to be 33.5 kJ/mol.

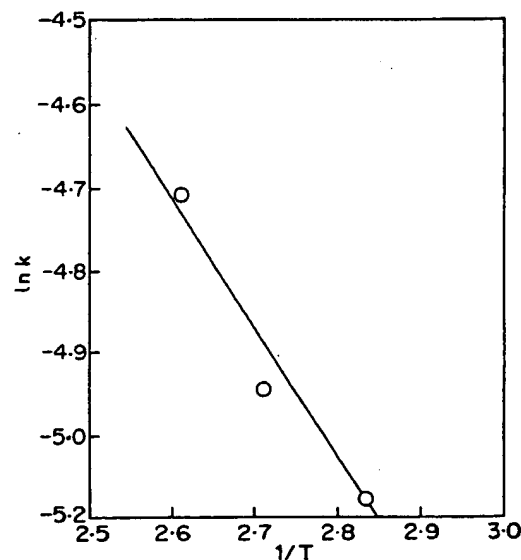


Fig. 9. Arrhenius plot.

6. Batch reactor model

The applicability of the rate model proposed was verified under integral conditions by using an isothermal batch reactor model to predict concentration–time profiles:

$$-\frac{dC_A}{dt} = R_A \quad (4)$$

Table 4
Fit of the rate model (Eq. (3))

T (K)	w (kg/m ³)	C_{A0} (kmol/m ³)	C_{W0} (kmol/m ³)	Initial rate (kmol/m ³ s $\times 10^4$)	
				Experimental	Calculated
353	10	2.77	0.00	0.30	0.31
	20	2.77	0.00	0.57	0.61
	20	4.44	0.00	1.30	1.40
	20	2.77	5.60	0.15	0.15
	20	2.77	22.2	0.048	0.045
368	10	2.77	0.00	1.00	0.80
	20	2.77	0.00	1.90	1.60
	20	4.44	0.00	2.90	3.30
	20	2.77	5.60	0.26	0.28
	20	2.77	22.2	0.074	0.082
383	10	2.77	0.00	2.20	2.00
	20	2.77	0.00	4.50	4.10
	20	4.44	0.00	7.00	7.05
	20	2.77	5.60	0.43	0.39
	20	2.77	22.2	0.12	0.11

$$-\frac{dC_A}{dt} = \frac{kwK_A C_A^2}{1 + K_A C_A + K_w C_w} \quad (5)$$

C_w , a time dependent concentration is expressed in terms of C_A using the stoichiometric relation:

$$C_w = [C_{A0} - C_A] + C_{w0} \quad (6)$$

where the subscript “0” denotes initial concentration for substrate and water. Substituting for the water concentration term in the rate equation, we get

$$-\frac{dC_A}{dt} = \frac{kwK_A C_A^2}{1 + C_A(K_A - K_w) + K_w C_{A0} + K_w C_{w0}} \quad (7)$$

The above equation was solved using Runge–Kutta method along with an optimisation program using the following boundary condition

$$C_A = C_{A0} \quad \text{and} \quad C_w = 0, \quad \text{at} \quad t = 0 \quad (8)$$

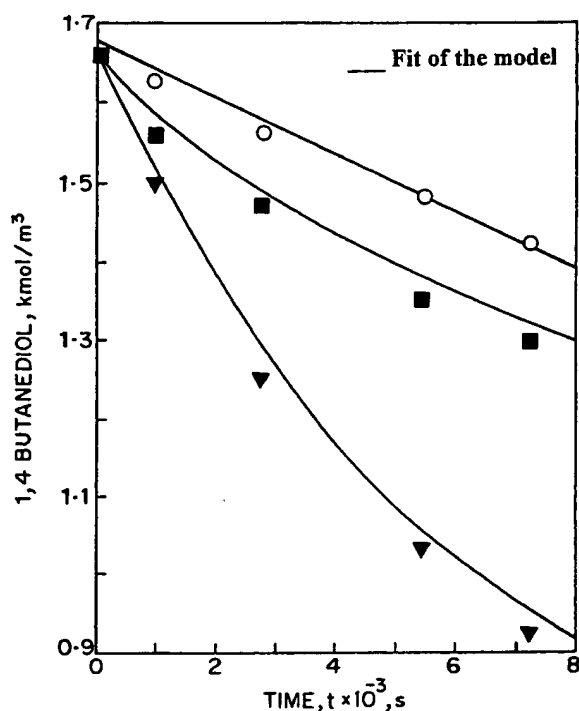


Fig. 10. Fit of the model to the experimental data (catalyst loading: 20 kg/m³; 1,4-butanediol concentration: 1.66 kmol/m³): (○) 353 K; (■) 368 K; (▼) 383 K.

The predicted concentration profiles match well with the experimentally observed concentration–time data. A typical fit of the model to the experimental data is shown in Fig. 10.

7. Conclusion

Dehydration of 1,4-butanediol was studied using a strong acid cation exchange resin: Indion-130 as a catalyst. The rate of dehydration varies directly with catalyst loading at all temperatures, confirming the absence of diffusional resistance. The initial rate shows variation of order more than one for substrate concentration. 1,4-Dioxane was found to be a better solvent than ethanol and water. The rate is strongly inhibited by the initial water present in the system. The inhibition is believed to be due to competitive adsorption of water on $-\text{SO}_3\text{H}$ groups of resin reducing the number of active sites. A kinetic model of the Langmuir–Hinshelwood type was found to represent well the intrinsic kinetics of dehydration of 1,4-butanediol to THF. The Arrhenius plot gave activation energy for this reaction as 33.5 kJ/mol. The rate equation was found to be applicable to the reaction system under integral conditions.

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